Appl. No. 10/740,073
Amdt. dated 1/5/07
Reply to Office action of 10/6/06

REMARKS/ARGUMENTS

Reconsideration of the application is requested.

Claims 9, 10, 12, 15-17 and 19-24 remain in the application.
Claims 9, 10, 12, 15-17 and 19-22 are subject to examination
and claims 23 and 24 have been withdrawn from examination.
Claim 9 and 23 have been amended. No claims have been added
or canceled herein.

In "Claim Rejections - 35 USC § 112," item 3 on page 2 of the
above-identified Office Action, claims 9, 10, 12, 15-17 and
19-22 have been rejected as being indefinite under 35 U.S.C.
§ 112, second paragraph.

More specifically, regarding claim 9, the Examiner questions
whether or not the sizing is optional in view of the wording
"not being provided with a sizing" and "being provided with a
sizing." The wording "at least one of the following being
true" was intended to indicate that the fibers could not be
provided with a sizing and/or be provided with a sizing
and/or be provided with a sizing as recited below, i.e.
waxes, etc. Accordingly, the word "or" has been added twice,
that is between the three paragraphs, making it clear that
the sizing is optional and the type of sizing can vary.

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The Examiner has also asked how the sizing relates to the
composition and if the sizing means viscose agent. Page 12,
second paragraph of the Specification of the instant
application makes it clear that the sizing which fulfills the
requirements of the present invention can be not only common
sizing used in textile processes (viscose agent), but also
all other substances mentioned as well (waxes, montan waxes,
waxes produced synthetically, low-viscosity pitches and
pitches dissolved in organic solvents).

In "Claim Rejections - 35 USC § 112," item 4 on pages 2-3 of
the Office Action, the Examiner has inquired as to whether
the term "at most" modifies only 4% or 8% as well. Claim 9
has been amended to make it clear that the latter is the
case. The 50% weight reduction between precursor fibers and
carbon fibers which occurs, is clear from the literature,
such the enclosed table on page 10 of Ullamann's Encyclopedia
of Industrial Chemistry, in the Chapter entitled: Fibers, 5.
Synthetic Organic.

In "Claim Rejections - 35 USC § 112," item 5 on page 3 of the
Office Action, the Examiner has stated that it is not clear
if the designations DIN 51930 and DIN 51909 do not change or
are well defined. The DIN Standards, which are the German
Industrial Standards, are well defined and universally

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accepted as such. Copies of these Standards are enclosed and include an English translation on the first page of each.

It is accordingly believed that the claims meet the requirements of 35 U.S.C. § 112, second paragraph. The above-noted changes to the claims are provided solely for clarification or cosmetic reasons. The changes are neither provided for overcoming the prior art nor do they narrow the scope of the claim for any reason related to the statutory requirements for a patent.

Finally, Applicant appreciatively acknowledges the Examiner's statement in "Response to Arguments," in item 7 on page 3 of the Office Action, that the rejections over the prior art appear to have been overcome.

It is also noted that the changes in claim 9 mentioned above have also been made in withdrawn claim 23. Accordingly, rejoinder of method claims 23 and 24 is requested as required by MPEP 821.04.

In view of the foregoing, reconsideration and allowance of claims 9, 10, 12, 15-17 and 19-24 are solicited.

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In the event the Examiner should still find any of the claims
to be unpatentable, counsel would appreciate receiving a
telephone call so that, if possible, patentable language can
be worked out.

If an extension of time is required, petition for extension
is herewith made. Any extension fee associated therewith
should be charged to Deposit Account Number 12-1099 of Lerner
Greenberg Stemer LLP.

Please charge any other fees that might be due with respect
to Sections 1.16 and 1.17 to Deposit Account Number 12-1099
of Lerner Greenberg Stemer LLP.

Respectfully submitted,
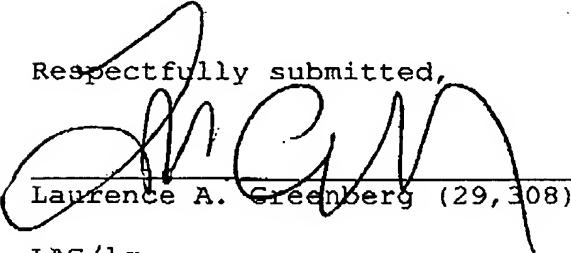
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January 5, 2007

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Fibers, 5. Synthetic Inorganic

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5. Carbon Fibers

Carbon fibers are black fibers used as yarns, felt, or powderlike short monofilaments with diameters smaller than 10 μm. They are mainly applied to reinforce polymers, much like glass fibers have been used for decades in fiber glass, with the principal difference that composites with carbon fibers are so-called *advanced composites* or *high-performance composite materials*. The progress achieved with carbon fibers, as compared with glass reinforcement fibers, is based on the superior stiffness of carbon fibers, combined with high strength and low density. As can be seen from Figure 42, the density of polyaramide fibers, introduced into the market nearly simultaneously with carbon fibers, is even lower, but strength and stiffness of these organic fibers do not reach near the top values for carbon fibers.
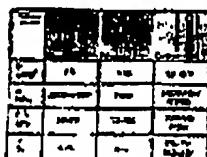
Figure 42. Comparison of the reinforcing fibers for advanced composites with polymer matrix: glass, polyaramides, and carbon

[Full View]

Figure 43 shows the superior specific stiffness (Young's modulus measured in fiber direction divided by the density) of various types of carbon fibers in comparison with those of polyaramide and glass fibers. The extremely low values for isotropic conventional metals and the theoretical maximum for the anisotropic graphite single crystal are also included. This figure demonstrates not only the superiority of carbon fibers but also the variability of stiffness among the various carbon fiber types. In the best case, up to 80 % of the theoretical modules of a graphite layer can be realized in a commercial material.
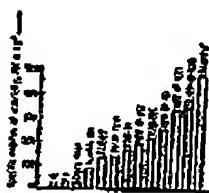

Figure 43. Specific tensile modulus (Young's modulus divided by density) of the various carbon fiber types (PAN and MPP) in comparison to other structural materials

* = single crystal (a-direction)
[Full View]

Nomenclature. Terms for description of new materials should be based on scientific characterization. Trivial terms, introduced locally, and still used, should be avoided. In UK and France the term *carbon fiber* is used correctly. In USA, however, the scientifically unjustified term "graphite fiber" is preferred in industry, and in German, as well as in Eastern European

languages, the tradition of describing carbon materials as coal has been carried over to the new material carbon fiber (German: *Kohlefaser*). The IUPAC has therefore established a sub-committee for description and characterization of carbon and graphite materials in general and of carbon fibers in specific. Some tentative recommendations for the terminology [87], partly still under discussion, are the following:

Carbon fibers are fibers (filaments, yarns, rowings) consisting of at least 92 wt % carbon, regularly in the nongraphitic stage, that is, with two-dimensional long-range order of the carbon atoms in planar hexagonal networks, but without any measurable crystallographic order in the third direction (c direction) apart from more or less parallel stacking.

HM-type carbon fibers are carbon fibers with a value of the modulus of elasticity in the fiber direction larger than 30 % of the elastic number c_{11} of a graphite single crystal, but with a ratio of tensile strength to tensile modulus below 1 %.

HT-type carbon fibers are carbon fibers with a value of the tensile strength above 3000 MPa and a ratio of strength to stiffness of ca. 1.5 – 2.0 %.

IM-type carbon fibers belong to the HT type carbon fibers because of comparable values of tensile strength but are characterized by improved stiffness (Young's modulus up to 30 % of the theoretical c_{11} value with remaining values of the ratio strength to modulus above 1 %).

In addition, the precursor material of the carbon fibers is important because the combination of various fiber properties and the behavior of the carbon fiber mechanically, physically, and chemically depend strongly on the raw material.

PAN-based carbon fibers are carbon fibers obtained from polyacrylonitrile (PAN) precursor fibers by stabilization treatment, carbonization, and possibly final heat treatment at even higher temperature.

Isotropic pitch-based carbon fibers are carbon fibers obtained from isotropic pitch fibers by stabilization treatment and carbonization.

Anisotropic pitch-based carbon fibers (MPP-based carbon fibers) are carbon fibers obtained from mesogenic pitch after this has been transformed into mesophase pitch (MPP) during the process of spinning, by stabilization of the spun mesophase pitch fibers, carbonization, and final heat treatment at even higher temperature.

Rayon-based carbon fibers are carbon fibers obtained from rayon precursor fibers by chemical pretreatment and carbonization. They are isotropic carbon fibers and can be transformed into anisotropic carbon fibers with high strength and stiffness by hot stretching above 2800 K.

Gas-phase grown carbon fibers are carbon fibers grown in a hydrocarbon atmosphere with the aid of fine particulated solid catalysts such as iron or another transition metals. They consist of graphitizable carbon and can be transformed into graphite fibers by heat treatment above 2800 K.

5.1. Properties
5.1.1. Mechanical Properties
The strength values differ dramatically among the various carbon fiber types. Because carbon fibers exhibit brittle fracture behavior, the strength: stiffness ratio strictly controls the fracture elongation (strain to failure) of the fibers. In Figure 44 these relationships are demonstrated graphically in three coordinates. The values of all commercially available carbon fibers are grouped around two areas, which describe opposing combinations of properties: the high modulus

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domains (HM-type fiber) and the high-strength, high-tenacity domains (HT-type fiber).
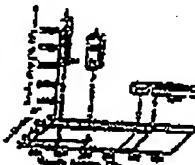

Figure 44. Characterization of the various commercial carbon fiber types by tensile strength and Young's modulus

HT = high tensile; IM = intermediate modulus; HM = high modulus; MPP = mesophase pitch-based high-modulus fibers
[Full View]

Nearly all carbon fibers available commercially have a near-circular cross section. As shown in Figure 45 the cross section of the carbon fibers mirrors the fiber precursor. Currently (1986) wetspun PAN is usually the raw material. Gasphase-grown carbon fibers exhibit the best graphitic order and preferred orientation, but have no importance for reinforcement.

Figure 45. Fracture surface of the precursor fibers (rayon, wetspun PAN, mesophase pitch) and of the resulting carbon fibers (REM)

Carbon yield given in wt %
[Full View]

5.1.2. Chemical Composition

Carbon fibers consist of elemental carbon. As all synthetic carbon materials, they are fabricated from carbon compounds by thermal degradation (pyrolysis), and the final (i.e., maximum) heat-treatment temperature controls the nature and amount of remaining ligand atoms in the residual carbon. The HM-type fibers consist of nearly pure carbon; however, the HT-types contain some nitrogen (<4 wt %) and oxygen (<1 wt %). Hydrogen contents can be neglected [88], [89].

Surface-treated carbon fibers contain, in addition, solid oxygen complexes on the surface and organic coatings (sizing), which protect the carbon fibers during handling and transport.

5.1.3. Structure

Solid elemental carbon has two equilibrium modifications: diamond with isotropic homopolar bonds between the carbon atoms and sp^3 hybridization of the electron levels and the hexagonal graphite with sp^2 hybridization, thus anisotropic structure. Rhombohedral graphite is a result of mechanical deformation of the hexagonal form. The broad variety of disordered carbons belongs to the graphitic modification mainly with sp^2 hybridization and thus a tendency to form planar polyaromatic molecules but with only two-dimensional order and no hexagonal ABAB-shaped arrangement of these polyaromatics in the third dimension. In this sense carbon fibers can be described as disordered carbon with more or less ordered polyaromatic layers and a hypermolecular anisotropic arrangement of these polyaromatics parallel to the fiber axis. Perfectness, size, and arrangement of these polyaromatics control the physical and especially the mechanical properties of the fibers. Partial sp^3 hybridization was confirmed in all artificial carbon, and especially in carbon fibers, and is explained by the carbon atoms on the edges and in disclinations of the polyaromatics [90], [91].

Transmission electron microscopy (TEM) produces bright field images of thin-layer cuttings of HT- and HM-type carbon and reveals the different degree of defect structure (Fig. 46) [90], [92].

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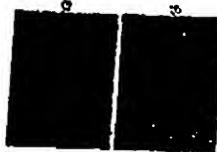
Figure 46.   TEM bright field images (cut perpendicular to the fiber axis) [90], [92]

A) Typical commercial HT type (T 300) B) HM type (SIGRAFIL HM) carbon fiber [Full View]

The preferred orientation in the direction of the fiber axis as indicated by the Ruland parameter q (0 corresponds to a statistic arrangement and −1.0 means completely preferred orientation) is shown in Figure 47 [93]. Some experimental fiber types based on mesophase pitch reach nearly 100 % of the theoretical Young's modulus, i.e., that of a single crystal. Such a preferred orientation is combined, however, with the disadvantage of low shear resistivity.

Figure 47.   Young's modulus of the various types of carbon fibers correlated with the degree of preferred orientation measured by X-ray diffraction and expressed by the Ruland parameter [93]

0 = statistical distribution, 1.0 = orientation of graphite single crystal [Full View]

The layer distance, which is easily measured, is a good indication of the degree of defect structure of a carbon fiber. Figure 48 shows the values for commercial fibers as received and the reduction of the $c/2$ value by further heat treatment, which heals structural defects [94].

Figure 48.   Main interlayer distances $c/2$ of various commercial carbon fibers and their decrease due to subsequent heat treatment. The $c/2$ values of graphitizable petroleum coke are included for comparison [92], [94], [95]

a) Ideal graphite; b) Petroleum coke; c) P55, MPP-based; d) AS4, PAN-based; e) T300, PAN-based; f) T800, PAN-based [Full View]

This healing process results in higher density and increased Young's modulus, which is shown in Figure 49 B. The strength passes a maximum at heat-treatment temperatures around 1500 °C (Fig. 49 A). The reduction of strength, with the minimum around 1800 °C, is caused by the escape of the remaining ligands, which causes severe structural disturbance. Only minor improvement takes place during further annealing. The variety of curves for PAN-based fibers is caused by differing oxidative pretreatment during the stabilization before carbonization [96], [137].
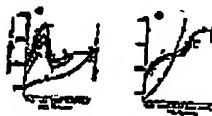
Figure 49.   The effects of heat posttreatment of carbon fibers [96], [137]

A) Tensile strength

SAF, stabilization treatment a) 230 – 260 °C/40 min; b) 230 – 270 °C/40 min; c) 230 – 290 °C/40 min; d) MPP

B) Young's modulusSAF, stabilization treatment a) 230 – 260 °C/40 min; b) 230 – 270 °C/40 min; c) 230 – 290 °C/40 min; d) MPP

Articles A/Fibers, 5. Synthetic Inorganic/5. Carbon Fibers

The effect of varied heat pretreatment during stabilization is included. For all PAN-based fibers, SAF precursor was used [137]. For comparison [96], the behavior of MPP carbon fibers is included.
[Full View]

Figure 50 shows the effects on the ultrastructure of heat treatment. The ordering process at the highest temperatures is easy to recognize for a commercial HT fiber by the enlargement of domains with parallel layer stacking (Figs. A and B). Such improvement of strength by annealing is not found in the case of pitch-based fibers with superior preferred orientation because of increased shear sensibility by annealing (Figs. 50 C and D). The much higher tendency of mesophase pitch-based fiber towards structural rearrangement can also be seen in Figure 50.

Figure 50. Effect of high-temperature heat treatment on the ultra structure and especially on the enlargement of the domains with parallel stacking of layers (TEM bright field of cuts parallel to the fiber axis)

A) PAN-based HT fibers (AS4W) as received; B) The same after-treatment at 2400 °C; C) MPP-based fiber (P55) as received; D) The same after treatment at 2440 °C
[Full View]

Based on electron microscopic studies, several models for structure in carbon fibers have been proposed. Four of these are shown in Figure 51 [97], [98], [99]. In all cases, parallel stackings of polyaromatic layers are arranged in the fiber direction in forms such as ribbons, plates, hoses, tubes, or combinations of the various structural elements.

Figure 51. Structural models of carbon fibers

A) Two-dimensional model proposed by RULAND [97] (ribbon model); stretched graphitized rayon-based fibers B) Three-dimensional model proposed by JOHNSON [98] (plate/sheet model); PAN-based fibers C) Ring/tube model proposed by OBERLIN [98] for all carbons resulting from thermal degradation of carbonizable solids [99] D) Hose-shaped layer stacking model proposed for highly heat-treated carbon fibers [99]
[Full View]

5.1.4. Physical Properties

Table 16 shows the densities, electrical resistivities, thermoelectric powers (TEP), magnetic susceptibilities, heat capacities, and thermal conductivities of the various carbon fiber types.

Table 16. Physical properties of typical commercial PAN-based carbon fibers.

Density, g/cm^3	Electrical resistance, 10^{-3} Ω m	TEP, μV/K	Susceptibility χ *, 10^{-6} emu/g	Specific heat Cp, J/gK	Thermal conduct. λ, W/mK

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			$\perp$	$\parallel$			
PAN-based HT	1.76–1.81	1.5–2.4	–1.6 to –2.4	–0.3	–0.05	0.71	8–20
PAN-based HM	1.82–2.00	0.6–1.0	17.2	–6.6	–0.63	0.71	60–100
Anisotropic pitch-based	2.00–2.15	0.4–1.1	22.6	–9 to –10.4	–0.70	0.93	110–375
Isotropic pitch-based	1.60	5–10		–0.74 to –5.32	–0.64 to –4.26		15

* Perpendicular ($\perp$) or parallel ($\parallel$) to fiber axis

The reversible thermal expansion is highly anisotropic (Table 17). In PAN-based HT-type carbon fibers high anisotropy is also found, as is the case for graphite single crystals. In contrast, the reported anisotropy in a mesophase pitch-based HM-type fiber is much smaller [100]. Experimental measurement for the direction perpendicular to the fiber axis, however, is very difficult, and a comprehensive study is still not available.

Table 17. Reversible thermal expansion of some commercially available carbon fibers.

	CTE $\alpha_\parallel$, 10^{-6} K^{-1}	CTE $\alpha_\perp$, 10^{-6} K^{-1}	$\alpha_\perp / \alpha_\parallel$
Graphite, single crystal	0.5–1.0	29	29–58
PAN-based HT	0.6	5–30	8.3–50
PAN-based HM	1.0	15	15
Anisotropic, pitch-based	0.9–1.4	6	4.3–6.7
Isotropic, pitch-based	3	3	1

Typical mechanical properties of carbon fibers are listed as a part of Figure 44.

5.1.5. Chemical Properties

The chemical resistivity of carbon and graphite materials against aqueous solutions and most chemicals at ambient temperatures is well-known and has been utilized in chemical apparatus. The behavior of carbon fibers is similar. Only fluorine acids as well as strong oxidants attack carbon fibers strongly. The tendency of graphite to form intercalation compounds with halogens, salts, oxidizing acids, and some other substances is also well-known. The majority of carbon fibers, which consist of nongraphitizable carbon is less susceptible to intercalation attack. Only gasphase grown fibers can be intercalated easily.

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Most destructive for carbon fibers are their reactivity with metals, above all aluminum at temperatures below 1000 K, and their reactivity with solid oxides at temperatures above 1000 K. This reactivity limits the use of uncoated carbon fibers for reinforcement of metals and oxides. However, if reaction and diffusion barriers are built in — silicon carbide, titanium nitride, and similar coatings have proved to be successful barriers (Fig. 52) —carbon fibers can be used to reinforce metals and oxides [101], [102].

Figure 52. SiC-coated carbon fibers in a SiO_2 glass matrix (parallel to the fibers) [101]

[Full View]

Solid surface oxides form as an intermediate stage before formation of volatile carbon oxides. Such solid surface oxide complexes improve the adhesion of carbon fibers in polymers and matrix in a composite [105], [106]. The thermal stability of surface oxides is limited to temperatures below 800 K for carboxylic groups and below 1000 K for nonacidic surface oxides. Figure 53 [103] shows the various types of surface oxides and their affinity to polar groups in the resins, which initiates at least chemisorptive adhesion and perhaps even formation of extensive chemical bonding between fiber and resin.


Figure 53. Oxide complexes on surface-treated carbon fibers and their affinity to polar groups in epoxy resins and curing agents [103]

[Full View]

The degree of adhesion is measured by interlaminar shear strength (Ilss). Figure 54 shows the effect of stepwise desorption of the surface oxides in surface-treated carbon fibers by heat treatment in argon and the resulting effects of such stepwise desorption on the remaining adhesion in an expoxy matrix. The strong improvement of adhesion in surface-treated HM fibers is associated with the carboxylic groups. The improvement of adhesion in HT-type fibers by surface treatment is much smaller, a maximum of 30 % of the total adhesion. The remaining adhesion in HT-type fibers is strongly correlated with the nitrogen content in the fiber. The adhesion of the fibers decreases abruptly if they are heat-treated above 1200 °C, which drives off the nitrogen remaining from the PAN precursor [88].

Figure 54. Gases (CO_2, CO) liberated during thermal desorption of surface-treated carbon fibers [89]

A) HM type, Sigrafil HM12S (Sign), 120 h oxidized in 68 % HNO_3

B) HT type, showing loss of nitrogen, content of PAN-based carbon fibers above 1000 °
C

a) T300S; b) T300U; S: surface treated; U: untreatedIlss = interlaminar shear strength
[Full View]

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The controlled formation of surface oxides can be attained by three routes:

1. Thermal oxidation at temperatures above 700 K
2. Wet oxidation in boiling nitric acid or in a similar oxidative liquid
3. Anodic oxidation in aqueous solution

Anodic oxidation is the only method used industrially for surface oxidation of carbon fibers. This process is the easiest to control and forms the greatest amount of surface oxides (Fig. 55).
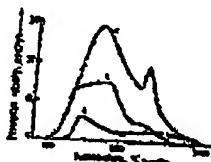

Figure 55. Amount of surface oxides formed by thermal, wet, and anodic surface treatment of HM fibers as measured by weight loss during thermal desorption in argon [104]

a) Thermal oxidation; b) in HNO_3 oxidized; c) anodic oxidation
[Full View]

Thermal oxidation, although simple to do, is dangerous because of the rapid reaction rate and the danger of fiber damage due to total oxidation. Figure 56 shows in an Arrhenius plot the experimental weight loss on oxidation of carbon fibers in air [104]. The HT-type fiber, which is given a maximum heat treatment at 1450 °C during fabrication, is much more sensitive to total oxidation than the HM-type fibers, which are heat treated above 2500 °C during fabrication. Total oxidation can be catalyzed even by alkali-metal compounds, as is the case for carbon and graphite materials. Heavy metal oxides are effective catalysts. Experimental results on the effect of copper oxide and vanadium oxide on the relatively resistant HM-type fibers are included in Figure 56. As a consequence, metallic impurities in carbon fibers have to be strictly avoided during industrial production.

Figure 56. Thermal oxidation rates of HM- and HT-type carbon fibers (Arrhenius plots), also showing the catalytic effects of heavy metal oxides on the oxidation of HM fibers [104]; r = rate constant

a) HM (Sigrafil); b) HT (Toho); c) HM + CuO; d) HM + V_2O_5
[Full View]

5.2. History
Public disclosures of practical processes for converting textile fibers into useful carbon fibers have been confined largely to the patent literature.

5.2.1. Rayon-Based Carbon Fibers
For rayon as the precursor material, a comprehensive survey was published by R. BACON [107]. One hundred years ago, EDISON [108] described an incandescent-lamp filament made by carbonizing a filament of natural and regenerated cellulose material. In the 1950s ABBOTT [109] developed a process for converting rayon into a fibrous carbon material for insulation, filtration, and absorption. This material was carbonized at temperatures up to 1000 °C and possessed tensile strengths of only 280 MPa. In 1959, Union Carbide [110], [111], [112] started commercial production of similar fibers, and other companies in the U.S.A. followed.

Various fiber types heat-treated at final temperatures around 1200, 1800, and even above 2500 °C

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have become commercially available, e.g., the carbonized VIB type and the WYB type heat-treated at graphitization temperatures, both from UCC (Union Carbide). The tensile strength of such fibers ranged from 300 to 700 MPa, while their moduli were between 30 and 50 GPa. The most important application was the reinforcement of phenolic resins to form ablative materials for rocket and missile components. This early period of carbon fiber production and application is reviewed by SCHMIDT and HAWKINS [113].

In these first years of the carbon fiber industry, several companies introduced a pretreatment process for the precursor fibers to increase carbon yields and speed up the processing rates, especially in the early heat treatment stage. The Pluton fiber of 3 M [114] was introduced in 1961. A decisive improvement of the mechanical properties of the carbon fibers was the plastic deformation of the fibers at temperatures above 2500 °C. This UCC process [115] led to the commercial production of the Thornell type, which had in 1965 a tensile strength of 1260 MPa and a modulus of 175 GPa (Thornell 25).

This was the period when the US Air Force Material Laboratory in Dayton, Ohio, strongly supported further development in the field of high-modulus carbon fibers [116], [117]. The goal was to replace boron fibers as soon as it proved possible to fabricate high-performance carbon fibers with a minimum modulus of 350 GPa. In 1970, UCC reached the goal with the commercially available Thornell 75 HM-type carbon fiber, which also had a Young's modulus of 500 GPa, a value corresponding to 50 % of the theoretical c_{11} value. Hitco [118] entered the market with yarns produced by similar methods. Although these carbon fibers were satisfactory in applications, the final decision of the market was to restrict use to the PAN-based carbon fibers.

5.2.2. PAN-Based Carbon Fibers

The history of PAN-based carbon fibers starts in 1950 with the observation of R. C. HOUTZ [119] that polyacrylonitrile fibers are converted into black, flameproof materials by heat treatment at 300 °C in air. However, products produced by this method were not used before 1959 [120]. At that time the discovery was made that flexible, flameproof textiles with the original fiber structure can be obtained only if the exothermic reaction between 150 and 300 °C is strictly controlled and if the high shrinkage during this thermal treatment is minimized by mechanical means. In 1960 the process to produce a flameproof fiber, starting with Dupont's AF Orlon fiber and commercialized as Black Orlon, was described in detail by VOSBURGH [121]. Heat treatment up to 15 h at 220 °C was needed to produce a well stabilized fiber with a strength of 40 % of the value of the original PAN fiber. The oxygen content of the final product was 10 – 20 wt %.

Surprisingly, this oxidizing-blackening treatment of the PAN fibers was not complemented by carbonization. Such a combination was first claimed by SHINDO [120] in 1959. A maximum tensile strength of 100 MPa was obtained. In 1965, JOHNSON, PHILIP, WATTS [122] added to this combined process the need to restrain shrinkage or alternatively to stretch the PAN fiber during stabilization treatment. They obtained carbon fibers with Young's moduli up to 420 GPa. This process is now the standard process for fabrication of PAN-based carbon fibers, although patent protection turned out to be limited and is completely gone today. A more detailed history is given by WATTS [123], and a complete literature survey is given by D. J. MUELLER [124].

5.2.3. Pitch-Based Carbon Fibers

The processes for carbon fibers from pitches are based on the observation of OTANI [125] in 1963 that some pitches are spinnable to pitch fibers, which can be converted into carbon fibers. Pitch from poly(vinyl chloride) turned out to be the best, but a variety of other pitches can be used after specified pretreatment as summarized by SUGIO OTANI and ASAO OYA [126]. The mechanical properties of the resulting carbon fibers were in the range 800 – 1800 MPa for tensile strength and 20 – 50 GPa for Young's modulus. These pitch-based carbon fibers were commercialized in 1970 by Kureha Chemical Industries and are still the only ones commercially available in the form of continuous yarns [127]. In 1985, FREEMAN [128] reported that the Ashland Company started

production of a variety of carbon fiber types using petroleum pitch as the raw material. Coal tar pitch is recommended as an alternative precursor material by ROMMEY [129]. All these pitch-based carbon fibers belong to the isotropic, low-modulus type.

Fabrication of anisotropic pitch-based carbon fibers with greatly improved mechanical properties was achieved by LEWIS and SINGER et al. [130] in 1976. This process is based on the mesophase, a liquid crystal formed within the pitch before spinning that enables the formation of a preferred orientation in the pitch fiber, thus also in the final carbon fiber. Values of tensile strength up to 3000 MPa and an extremely high Young's modulus, up to 600 GPa, can be achieved.

Laboratory developments have continued in many countries of the Western World. Commercial products are available from AMOCO (previously Union Carbide) [131].

5.2.4. Vapor-Grown Carbon Fibers

Whiskers and needles of carbon deposited from the gas phase were described in 1966 by FITZER and SCHLESINGER [132]. FITZER and RHEE [133] continued these studies and reported in 1970 growth rates and mechanical properties of the whiskers and needles. Tensile strengths up to 1500 MPa and stiffness values up to 300 GPa were reported. The decisive progress was reported by ENDO [134] in 1974 when he recognized that the whisker growth follows a catalytic mechanism starting from fine, dispersed solid metal particles in the substrate. Whisker lengths up to 250 mm and tensile strength values up to 26 000 MPa have been reported so far by ENDO [134]. Commercialization has not been announced, however, probably because of the completely different structure of vapor-grown carbon fibers. These consist of soft carbon, that is, the graphitizable less-disordered variety. Therefore, high mechanical properties cannot be expected. They are most suitable for intercalation (high electrical conductivity).

5.3. Production

All commercial production processes for carbon fibers are based on carbonization of polymer fiber precursors. The preconditions for useful fiber formation compiled in Table 18 must be fulfilled. Thus, the number of suitable polymer fibers is limited. The fiber form is always preserved during carbonization in the case of nonmeltable polymers, such as thermosetting resins, which can be thermally degradated directly. Thermoplastic precursor fibers have to be converted into a nonmeltable form before carbonization. This is called stabilization treatment and occurs on conversion of the linear polymers into ladder polymers and on formation of additional cross-linkages. In the case of pitch precursor fibers, the melting of the mixture of polyaromatic compounds must be hindered by oxidation. Three precursor materials are satisfactory: (1) rayon fibers, (2) PAN fibers, and (3) pitch fibers. Rayon fibers do not require stabilization, only preimpregnation is necessary to improve the carbon yield. PAN and pitch fibers need stabilizing pretreatment. The carbon yield is lowest for rayon fibers and highest for stabilized pitch fibers:

Rayon fibers	25 %
Oxidized pitch fibers	80 %
Polyacrylonitrile	50 %
Oxidized pitch	up to 80 %
Phenolic and furan resins	up to 85 %

Table 18. Restrictions on the precursor fiber for carbon fiber fabrication

Preconditions for carbon	Parameters

fiber

manufacture

	Precursor	Process
Preservation of the fiber form of the polymer	thermosetting or thermoplast fibers	direct thermal degradation or stabilization treatment of meltable precursor before thermal degradation
High carbon yield	selection of the polymers	optimization of the stabilization and carbonization parameters
Preferred orientation of the polycarbon layers with highest degree of defects in the ultra structure	highly cross-linked, unmeltable polymers	stretching of the precursor before or during stabilization and/or hot-stretching of the carbon fiber

The most important parameter in producing high-quality carbon fibers is the preferred orientation of the polyaromatic layers parallel to the carbon fiber axis. Only then can the high strength of the bonds in the molecular structure of the graphite lattice ($c_{11} = 1060$ GPa, $c_{33} = 33$ GPa) be transferred into stiffness and strength of the carbon fiber. The low shear modulus in the graphite crystal structure ($c_{44} = 4.6$ GPa) must be avoided by having the highest degree of defects in the ultrastructure of the carbon fiber. In the case of rayon precursor fibers the needed high degree of structural imperfectness can be realized, however the preferred orientation is realizable only by hot working of the carbon fiber at 3000 K. This hot stretching process is difficult to carry out on an industrial scale. Therefore, carbon fibers are no longer produced from rayon.

In PAN- and pitch-based anisotropic carbon fibers, the preferred orientation is introduced into the precursor before carbonization. Polyacrylonitrile is the most important precursor material. More than 90 % of all commercially produced carbon fibers that are used for reinforcement of polymer material are based on this polymer. Only a minor part is produced from pitch.

5.3.1. PAN Precursor Fiber

Textile PAN fibers usually consist of ternary mixtures of copolymers with 89 – 95 wt % acrylonitrile (AN), 4 – 10 wt % of a non-ionogenic comonomer plasticizer, and 1 wt % of additive to chemically bond dyes [135]. For the precursors for carbon fibers, a lower content of comonomers, usually below 3 wt %, is used.

Polymer fibers can be spun by melt, wet, and dry spinning processes. In the case of polyacrylonitrile as a carbon fiber precursor, the wet spinning process is the most important. In 1986 a new melt spinning process was presented which would offer economic advantages [136].

The solvents dimethylformamide (DMF) and dimethylacetamide (DMA) are usually preferred for wet spinning today. For carbon fiber precursors, however, the inorganic solvents nitric acid, stannum chloride and thiocyanate are also used. In any case, copolymer composition of the precursor, the spinning technology, and especially the solvent are almost always strict commercial secrets. Only Courtaulds (United Kingdom) describes the use of dimethyl sulfoxide for fiber

precursor fabrication.

The main difference between textile PAN fibers and PAN precursor fibers is the different degree
of stretching: the stretching ratio for textile fibers is 1 : 2 to 1 : 10, that for PAN precursor fiber
1 : 12 or more. There is the danger of overstretching, which introduces defects into the polymer
fiber that initiate defects in the carbon fibers, thus causing low strength.

The extremely high-strength and high-tenacity carbon fibers are mainly produced from precursors
more carefully spun and stretched to a higher degree. Dry-jet wet spinning would be a good
method for this.

5.3.2. Stabilization

Polyacrylonitrile is a thermoplastic polymer that decomposes above 370 °C. A suitable
stabilization process is needed before carbonization to obtain an infusible intermediate that
preserves the orginal fiber structure. This intermediate is known as inflammable textile (e.g.,
PAN-Ox).

The stabilization step is the most important one from the viewpoint of carbon fiber quality and
process economy. The reaction is diffusion controlled, and a residence time of ca. 1 h at
temperatures between 200 and 280 °C is needed. Fiber shrinkage during stabilization must be
avoided (see SectionPAN-Based Carbon Fibers).

The chemistry of the stabilization process is illustrated schematically in Figure 57. The
thermoplastic chain is cyclized to a naphthyridine ring system and simultaneously dehydrated in
the backbone to form conjugated double bonds. The resulting aromatic polymer has ladder units
of about five, corresponding to the average number of isotactic sequences in the nitrile polymer.
Cyclization can occur with or without simultaneous dehydrogenation as shown in Figure 58
[137]. In both cases strong exothermic reactions are observed. In industrial processes, cyclization
is always carried out in an oxidizing atmosphere because of the much higher carbon yield during
the subsequent carbonization [139].

Figure 57. The chemistry of stabilization and carbonization: fabrication from
homopolymer PAN and stabilized PAN [137], [138], [147]

[Full View]
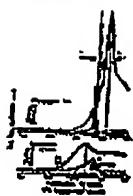
Figure 58. The exothermic stabilization in nitrogen (cyclization) and in air (cyclization
and dehydrogenation) as revealed by DSC (differential scanning calorimetry) [137]

[Full View]

There is a direct correlation between the amount of oxygen absorbed and the density of the
stabilized fiber. The best mechanical properties result for a precursor density of $1.4 - 1.42$ g/cm^3,
which corresponds to oxygen contents of $10 - 14$ wt % (Fig. 59).
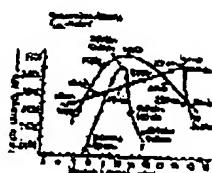
Figure 59. The effect of oxygen uptake during stabilization on the strength of the final carbon fiber

a) 230 °C isotherm/air; b) 230 °C isotherm, 1st stage N$_2$, 2nd stage air; c) 230 → 270 ° C nonisotherm/air [Full View]

The stabilization causes the color to change from the white of polyacrylonitrile to yellow and brown and finally to the black of the intermediate, the oxidized, inflammable polyacrylonitrile. The stabilization chemistry has been treated comprehensively in numerous papers, e.g., [137], [138], [140], [141], [142], [143], [144], [145], [146], [147].

5.3.3. Process Parameters

The carbonization step can be carried out much faster than the stabilization step; however, the evolution of the volatile byproducts, mostly H$_2$O, HCN, CO$_2$, and N$_2$, must be taken into account [148].

Practical temperature – time profiles have been published [137], [142], [149], [150], [151]. The quality of the final carbon fiber product is controlled by the precursor fiber, the stabilization treatment and the oxygen content, and finally by the carbonization schedule.

An example of a continuous stabilization and carbonization for fabrication of carbon cloth from PAN from patent literature is shown in Figure 60 [152].

Figure 60. Hitco process for production of carbon cloth from PAN cloth showing temperature and tension profiles [152]

[Full View]

5.4. The Pitch Fiber Process

5.4.1. Isotropic and Anisotropic Pitch Fiber Precursors

Carbon fibers made from pitch precursor are available with isotropic or anisotropic structure, the former made from isotropic pitch, the later from mesophase pitch. The isotropic pitch-based carbon fibers have low mechanical properties. They have been produced industrially from coal tar pitch by Kureha (Japan), for more than 15 years. The petroleum pitch producer Ashland (United States) manufactures isotropic carbon fibers, which are used mostly for thermal and mechanical insulation but also as fillers.

Anisotropic carbon fibers, which can be used for reinforcement because of their excellent mechanical properties, are produced in a process that takes advantage of the larger planar polyaromatic molecules in pitch and their tendency to form liquid crystals with parallel polyaromatic layers. The mesophase pitch is melt spun and stretched in the plastic deformable stage to produce pitch fibers with preferred orientation.

All pitch fibers must be stabilized before carbonization, but pitch fibers with preferred orientation consisting to a large extent of mesophase not only hinder melting during carbonization but also cross-link the polyaromatics upon oxidation thus hindering formation of graphitized carbon fibers.
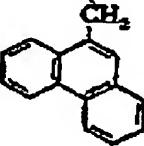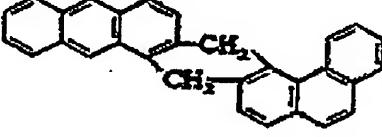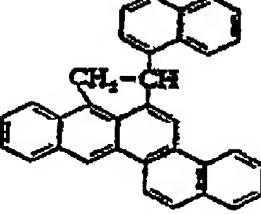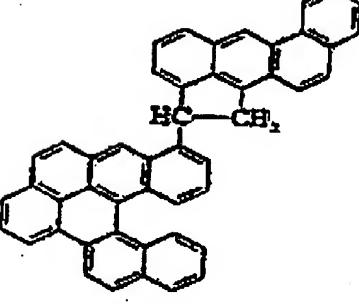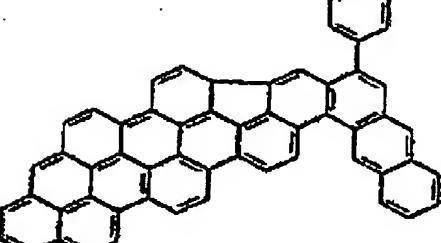
5.4.2. The Mesophase Formation

Pitch is the residue from distillation of coal tar or crude oil or from cracking hydrocarbons. All pitches consist of thousands of aromatic hydrocarbons along with more or less cyclic aliphatics and aliphatic side chains. The molecular mass of the polyaromatic compounds ranges between 200 and 800. All the compounds in a single pitch have never been identified. Pitches are characterized by fractionation: their solubility in a sequence of standard solvents (Table 19). The model molecules shown in the table are suggested by comprehensive analytical investigations [153]. The melting points of the various pure compounds cover a range of hundreds of degrees. Pitches, however, form multi-eutectic systems with softening temperatures between 50 and 300 ° C, much lower than the melting temperatures of the pure aromatic components.

Table 19. Characterization of typical coal tar and petroleum pitches by solvent fraction and model molecular structures for the fractions [153]
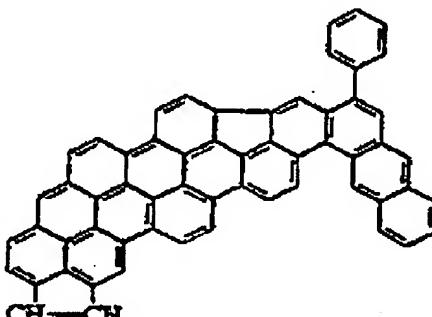
wt%	Coal tar pitch		w
52.2		$MW = 268$ $C/H = 1.31$ $\frac{H_{arom}}{H_{aliph}} = 7$ $\frac{C_{arom}}{C_{aliph}} = 20$	6;
7.8		$MW = 380$ $C/H = 1.5$ $\frac{H_{arom}}{H_{aliph}} = 4$ $\frac{C_{arom}}{C_{aliph}} = 14$	11
1.6		$MW = 429$ $C/H = 1.6$ $\frac{H_{arom}}{H_{aliph}} = 6.3$ $\frac{C_{arom}}{C_{aliph}} = 16$	9
5.8		$MW = 602$ $C/H = 1.48$ $\frac{H_{arom}}{H_{aliph}} = 7.6$ $\frac{C_{arom}}{C_{aliph}} = 23$	2
3.4		$MW = 737$ $C/H = 2.03$ $\frac{H_{arom}}{H_{aliph}} = 6.3$ $\frac{C_{arom}}{C_{aliph}} = 29$	

wt%	Coal tar pitch	
3.4		$MW = 737$ $C/H = 2.03$ $\dfrac{H_{arom}}{H_{aliph}} = 6.3$ $\dfrac{C_{arom}}{C_{aliph}} = 29$
19.7		$C/H = 2.14$
9.5		$C/H = 2.90$

The mesophase is formed during thermal degradation in the temperature range 400 – 450 °C and is controlled by the hydrogen content remaining in the aromatics during this heat treatment. Aromatics with an average molecular mass around 800 (coal tar pitches) and aromatics with aliphatic side chains and a molecular mass around 1000 (petroleum pitches) are able to form nuclei for discotic liquid crystals [153].

The liquid crystals in pitch are spherical with the molecular orientation shown in Figure 61. The coalescence of these liquid crystals with disklike molecules is similar to that of the liquid crystals with rodlike molecules.

Figure 61. The coalescence of discotic liquid crystals in pitch

[Full View]

From the viewpoint of the phenomenology, the formation of liquid crystals is similar to that of crystallization, starting from observable nuclei with diameters larger than 1 μm. The growth and coalescence proceed until all isotropic pitch matrix is consumed. Insoluble impurities in the molten pitch matrix (primarily quinoline insolubles, i.e., the pitch residue) inhibit coalescence and therefore also the formation of large volumes of anisotropy.

5.4.3. Process Steps

The viscosity of pitch, a precondition for satisfactory melt-spinning behavior, is determined by pitch composition. Figure 62 shows the apparent viscosities of a typical petroleum pitch and a

typical coal tar pitch as functions of heat treatment [154]. The behavior of toluene-soluble (TS) and toluene-insoluble (TI) fractions of the coal tar pitch and of two mixtures of TS and TI fractions are included. Softening of the pitches upon heating is indicated by viscosity decrease; solidification due to mesophase formation, by viscosity increase. Spinning is difficult for high mesophase contents (which produce the HM fibers), however carbon yield increases with viscosity (Fig. 63) [154]. These contradicting conditions cause technological problems.

Figure 62. Apparent viscosity (rotation viscosimeter) of the petroleum pitch A240, the purified coal tar pitch SP80, fractions resulting from toluene extraction of SP80 (TS = toluene soluble, TI = toluene insoluble), as well as two mixtures of TS and TI [154]

[Full View]
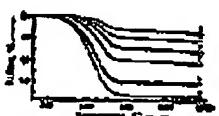
Figure 63. Carbonization residues from the pitch samples described in Figure 62 [154]

a) Toluene soluble; b) SP80 and 4 : 1 mixture; c) 1 : 1 mixture; d) 1 : 4 mixture; e) 1 : 9 mixture; f) toluene insoluble
[Full View]

Stabilization is carried out between 200 and 300 °C [155], much like in the PAN process. The stabilization times are dramatically shorter, however, between 10 and 30 min. The patent literature indicates that commercial pitch-based carbon fibers are given a final heat treatment around 1800 °C (P55 type). Fiber types with a relatively high Young's modulus, in the area of 400 GPa, can be achieved (cf. Fig. 44). A flow sheet for the entire fabrication process is given in Figure 64 [156].
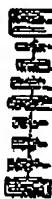
Figure 64. Flow sheet for manufacture of carbon fibers from pitch (Union Carbide Corp. (UCC) process) [156]

[Full View]

5.5. Comparison of the Carbon FibersBased on PAN and on Pitch

Figure 65 shows the stress – strain behavior of PAN-based carbon fibers, as commercially available, of the intermediate modulus fibers in development, and of isotropic and anisotropic pitch-based fibers.

Figure 65. Stress – strain behavior of commercially available PAN- and pitch-based carbon fibers

[Full View]

The pitch process for carbon fibers potentially offers the capacity to produce carbon fibers

covering the whole mechanical property range of the carbon fiber family. However, these expectations for pitch-based fibers have not yet been realized in spite of worldwide, intensive research.

The overwhelming part of commercial carbon fibers is the PAN-based HT type. High strain-to-failure of the fibers is seen as one of the key properties for the fracture toughness needed for broader application of advanced composites. The best strain values, between 1.5 and 2 %, are possible on industrial scale only with PAN-based HT-type fibers. Further, manufacturing problems are reduced if fabrication starts from a fully synthetic precursor material, with strictly controlled quality, instead of from a semi-natural raw material, such as petroleum or coal tar pitches, with strongly varying compositions depending on crude or coal type and the thermal history.

The applications of ultrahigh modulus carbon fibers from anisotropic pitch will most likely remain restricted to space structures and to carbon fiber-reinforced carbon fiber material (carbon – carbon composites). The challenge to increase the applications of anisotropic pitchbased carbon fibers can be satisfied only if production of medium-quality fiber types can be coupled with further drastic price reductions.

5.6. Commercial Availability and Economic Aspects
5.6.1. Companies and Trade Names

In the 1960s, the industrial production of carbon fibers started in UK, Germany, Japan, and USA with a total volume below 1000 t/a. Very soon, however, Japan had the advantage because of the availability of PAN-fiber plants using the wet process, whereas in USA and Germany PAN was produced mostly by the older dry process. Two Japanese companies specializing in the production of synthetic fibers, namely Toray and Toho Beslon, have succeeded in greatly expanding carbon fiber production. Today, these two companies dominate the world's carbon fiber production by licenses and joint ventures.

Hercules (USA) is independent from the two Japanese companies, but works jointly with Sumitomo, another Japanese PAN-precursor producer. Courtaulds fabricates precursors and is thus independent from Japanese imports. It is also the only company that sells PAN-precursor fibers suitable for a carbon fiber manufacture the world over without the limitations of licenses or joint ventures. In Germany, Sigri is independent, but fabricates no precursors. The producers, their production, their trade names, and some commercially available carbon fiber types from PAN precursors are compiled in Table 20.

Table 20. Carbon fiber producing companies, trade names, and commercial availability in the world market.

Producer (country)	Production capacity, t/a state 1988	Trade name	Types			Licensed by
			HT	IM	HM	
Toho (Japan)	1380	Besfight	HTA ST 3	IM 400 IM 500	HM 35 HM 40 HM 45	
Toray (Japan)	1500	Torayca	T 300	T 800	M 30	Asahi

Producer	Capacity	Trade name				Source
			T 700	T 1000	M 40	Nippon (Japan) 300
Amoco (USA)	360	Torayca	T 300	T 800	M 50 / M 30	Toray
Hercules (USA)	1360	Magnamite	T 700 / As 4	T 1000 / IM-6	M 40 / M 50 / HMS	Toray
			As 6	IM-7 / IM-8	HMU	
BASF (USA)	450	Celion	G 30 – 400	G 40 – 600	G 50 – 300	Toho
			G 30 – 500	G 40 – 700	Gy 70	
			G 30 – 600		Gy 80	
Hysol (UK + USA)	700	Grafil	XA-S	IM-S	HM-S	
Sigri (FRG)	100 (PANOX 400)	Sigrafil	C	—	+	
AKZO (FRG + USA)	860	Tenax	HTH			Toho
Soficar (F)	300	Filkar	ST 3 / T 300 / T 400	T 800	M 30 / M 40 / M 50	Toray
Amoco (USA)	230 *	Thornel		P 55	P 75 / P 100 / P 125	
Mitsubishi Chem. Ind.	500 *	Dialead				
Ashland (USA)	140 *	Carboflex	types	isotropic		
Kureha (Japan)	900 *		types	isotropic		

* pitch-based carbon fiber types

5.6.2. World Capacity

The world capacity to produce carbon fibers is estimated to exceed 5000 t/a, and is increasing rapidly. The development of world production capacity during the last 15 years is shown in Figure 66. The small quantities of anisotropic and isotropic pitch-based carbon fibers are

http://wedcs410.sglcarbon.eu:85/wiley/lpext.dll/Ullmann-1/all_001/sect5.html   30.11.2006

PAGE 31/47 * RCVD AT 1/5/2007 8:54:05 AM [Eastern Standard Time] * SVR:USPTO-EFXRF-6/35 * DNIS:2738300 * CSID:+9549251101 * DURATION (mm-ss):06-48

included. There is disequilibrium between capacity, production, and real consumption, but more exact information is not available. It is estimated that capacity will grow up to 10 000 t/a and increase between 30 and 50 % per year.
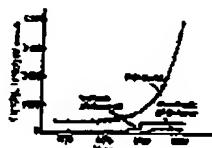

Figure 66. World production capacity for carbon fibers

[Full View]

Average prices of carbon fibers are shown in Figure 67. The price for PAN-based carbon fibers strongly depends on the number of filaments in one tow. The so-called low-filament tows, with 3000 monofilaments, have been used for years. Currently (mid-1980s) most prepregs use tows with 6000 monofilaments. The tendency is to try to increase the filament number up to 12 000.
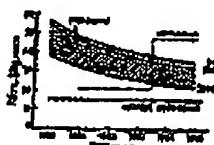
Figure 67. The development of carbon fiber prices

[Full View]

PAN-multifilament tows are the cheapest form of PAN-based carbon fibers: continuous 320 000 monofilament tows as used in textile application are difficult to handle in high-performance composites. They are mainly used for cutting into chopped fibers. However, multifilament tows with only 40 000 monofilaments have been introduced. The technological gap between the low filament tows (12 K and increasing) and the multifilament tows (40 K and decreasing) is diminishing. This should result in lower prices.

The price situation for anisotropic pitch-based carbon fibers is complicated. Around 1981 Union Carbide started to produce high-quality carbon fibers and sell them at $ 20 per kg, much below the price of PAN-based fibers at that time. As shown in Figure 67, the market situation and production difficulties forced the producer in 1983 to more than double the price. Anisotropic pitch-based high-modulus fibers are now much more expensive than PAN-based HT fibers.

The price situation is stable for isotropic pitch-based carbon fibers as delivered by Kureha for decades. Ashland, the Major petroleum pitch producer, has entered the market.

5.7. Future Importance

As has become evident over the last decade, polymers reinforced with carbon fibers present the opportunity not only to replace but also to displace structural metals [157]. The advanced composites (carbon fiber-reinforced plastics, CFRPs) are superior to conventional metals in respect to strength, stiffness, lightness, thermal expansion, fatigue, and corrosion resistance (Fig. 68).

Figure 68. The technical advantages of CFRPs over conventional metals

[Full View]
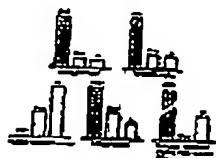
Comparable Costs. The comparable costs of strength and stiffness of a unit volume of an advanced composite reinforced with PAN-based HT or HM carbon fibers, polyaramide fibers, glass fibers, former boron, or silicon carbide fibers have been estimated and compiled in Table 21.

Table 21. The price related to specific tensile strength and specific stiffness.

Fiber type	Price, DM/kg	Density, 10^3 kg/m^3	Price divided by specific	
			Tensile strength, DM/ 10^4 kgm	Young's modulus, DM/ 10^4 kgm
E glass	10	2.50	1.5	0.07
Kevlar	40	1.45	2	0.05
C_{PAN} (HT)	70	1.75	3	0.05
C_{MPP}	200	1.99	17.5	0.19
C_{PHN} (HM)	450	1.85	27	0.30
B/c	1000	2.50	67	0.50
SiC/c	4000	3.50	400	3

From the viewpoint of strength, the glass fiber reinforcement is cheapest, followed by polyaramide and PAN-based HT fibers. PAN-based HM fibers are much more expensive. The CVD boron and silicon carbide fibers cannot be considered on an economical basis. From the viewpoint of stiffness, the carbon fiber-reinforced composites, although attractive on a price basis, are limited to the low modulus range.

Technological Fields. The aerospace field can expect the highest technical and economic benefit from application of these new materials. In the past such risky innovations were the only chance to realize some ambitious projects. The U.S. space shuttle is the best example. Although NASA designed this shuttle in the early 1970s essentially in conventional materials, it was not realizable without carbon fiber-reinforced doors for the loading room. In this way, carbon fiber-reinforced epoxies were tested in practice and accepted as performing structural materials for primary

structures in manned flying vehicles. Today, military aircraft contain up to 50 wt % carbon-reinforced resins instead of light metals like aluminum. Commercial aircrafts are following step by step to replace aluminum by carbon fiber-reinforced composites.

The cost-benefit schedule of typical composite applications is:

space market	5 000 €/kg
air craft	500 €/kg
racing car	50 €/kg
automotives	up to 5 €/kg

The present calculation gives load savings of 15 – 30 % in aircraft and component costs of 77 – 150 €/kg. In automotives, load savings of 20 – 50 % but component costs up to 2.6 €/kg. Although the cost-benefit ratio is lowest in automotive applications, this field is the most promising for the future. To produce large cars with extremely light weight using the design rules of the aerospace industry presents a real challenge to the auto industry. The question becomes more and more a question of economy of scale for the fiber production on the one hand, and of rationalized processing for final products on the other. Plans for future production lines have already been published [158].

Another argument supporting a shift from metals to carbon fiber-reinforced composites is the energy requirements shown in Table 22 [159]. The numbers in the table include both the energy needed to process the materials and to process the raw material. The composites appear advantageous in terms of volumes and even more so in terms of mechanical properties per unit volume.

Table 22. Energy requirement in kWh for the production of Al, Fe, CFRP's and PVC [159].

Material	Density, $\frac{g}{cm^3}$	Energy requirement for production		
		$\frac{kWh}{kg}$	$\frac{kWh}{L}$	$\frac{kWh}{L}/\frac{N}{mm^2}$
Al	2.8	37.3	104.5	232.2
Fe	7.9	6.8	53.6	26.8
CFRP (UD)	1.5	3.7	5.6	3.5
CFRP (2D)	1.5	3.7	5.6	6.9
PVC	1.4	7.9	11.1	1110.0

PREVIOUS NEXT

Articles A/Fibers, 5. Synthetic Inorganic/5. Carbon Fibers

DEUTSCHE NORM April 2006

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Ersatz für
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Prüfung von Kohlenstoffmaterialien –
Herstellung von stranggepressten Probekörpern aus kalzinierten Koksen –
Feststoffe

Testing of carbonaceous materials –
Preparation of extruded samples of calcinated cokes –
Solid materials

Essai des produits carbonés –
Préparation d'échantillons extrudés à partir de cokes calcinés –
Matériaux solides

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Vorwort

Die vorliegende Norm wurde vom Arbeitsausschuss NMP 281 „Prüfverfahren für Kohlenstoff und Graphit" ausgearbeitet.

Änderungen

Gegenüber DIN 51930:1989-09 wurden folgende Änderungen vorgenommen:

a) Presshilfsöl statt Stearinsäure eingesetzt;

b) Durchmesser der Proben 10 mm bis 25 mm;

c) Änderung der Kornfraktion;

d) Änderung der Temperaturen;

e) Korrektur der Aufheizrate beim Graphitieren.

Frühere Ausgaben

DIN 51930: 1989-09

2

1 Anwendungsbereich

Das Verfahren nach dieser Norm dient der Herstellung von Probekörpern aus kalzinie:
Folgenden Text kurz „Koks" genannt) unter Verwendung zweier verschiedener Kokskörnungen

An den geglühten oder graphitierten Probekörpern werden Eigenschaftswerte, wie z. I
thermische Ausdehnungskoeffizient, der spezifische elektrische . Widerstand oder die
gemessen. Die gemessenen Werte dienen der Qualitätsbeurteilung der Kokse.

2 Normative Verweisungen

Die folgenden zitierten Dokumente sind für die Anwendung dieses Dokuments erforderlich
Verweisungen gilt nur die in Bezug genommene Ausgabe. Bei undatierten Verweisungen
Ausgabe des in Bezug genommenen Dokuments (einschließlich aller Änderungen).

DIN 12880-1, *Elektrische Laborgeräte — Wärmeschränke — Teil 1: Sicherheitstechnische Anfo
Prüfungen; Allgemeine technische Anforderungen*

DIN 12880-2, *Elektrische Laborgeräte — Wärmeschränke — Teil 2: Prüfung*

E DIN 12880, *Elektrische Laborgeräte — Wärme- und Brutschränke*

DIN 51701-2, *Prüfung fester Brennstoffe — Probenahme und Probenvorbereitung — Dur
Probenahme*

DIN 51701-3, *Prüfung fester Brennstoffe — Probenahme und Probenvorbereitung — Dur.
Probenvorbereitung*

DIN 51920, *Prüfung von Kohlenstoffmaterialien — Bestimmung des Erweichungspunktes ne
Binde- und Imprägniermittel*

DIN 52025, *Prüfung von Kohlenstoffmaterialien — Bestimmung des Erweichungspunktes n
Sarnow*

DIN ISO 3310-1, *Analysensiebe — Technische Anforderungen und Prüfung — Teil 1: Anal,
Metalldrahtgewebe*

3 Kurzbeschreibung

Eine Probe des Kokses wird zerkleinert und in einer Labormischmaschine unter Zusatz vo
Eisen(III)-oxid und Presshilfsöl heiß gemischt. Die Mischung wird mit einer Strangpresse zu Pro
einem Durchmesser von 10 mm bis 25 mm verpresst. Die Probekörper werden entweder in ein
vorgeglüht (Endtemperatur 850 °C) und in einem Hochtemperaturofen graphitiert (Endtemper,
oder in einem Muffelofen geglüht (Endtemperatur 1 300 °C).

4 Geräte und Hilfsstoffe

a) Labormühle zum Mahlen von Koksen;

b) Siebeinrichtung;

DIN 51930:2006-04

c) Analysensiebe aus nicht rostendem Stahl mit einem Drahtsiebboden: 6,7 mm – 3,35 mm – 2,36 mm – 1,18 mm – 0,85 mm – 0,5 mm – 0,425 mm – 0,075 mm und 0,071 mm (siehe DIN ISO 3310-1);

d) Waage mit einer Fehlergrenze $G = 0,1$ g;

e) Wärmeschrank, mit dem eine Temperatur von (200 ± 5) °C eingehalten werden kann, z. B. Wärmeschrank nach DIN 12880-1, DIN 12880-2 oder E DIN 12880;

f) Labormischmaschine, nutzbares Volumen mindestens 1 l, mit der das zu mischende Material erhitzt und bei einer Temperatur von (165 ± 5) °C gemischt werden kann;

g) hydraulische Strangpresse, bestehend aus folgenden Teilen:

   — Hydraulikanlage, ausgelegt für einen Pressdruck von etwa 200 bar,

   — Massezylinder mit einem Durchmesser von etwa 50 mm, einer Länge von etwa 560 mm, schwenkbar um 90° von der horizontalen in die vertikale Richtung und einer Heizung zum Erhitzen des Massezylinderinhaltes auf (125 ± 5) °C,

   — Mundstück mit einem Durchmesser des Mundstückauslaufes von 10 mm bis 25 mm und einer Heizung zum Erhitzen des Mundstückes auf (105 ± 5) °C,

   — Vorrichtung (Vorpressplatte) zum Verschließen des Mundstückes bei der Vorverdichtung (siehe Anmerkung zu 6.3);

h) elektrisch beheizter Muffelofen, mit dem eine Aufheizgeschwindigkeit von etwa 100 K/h und eine Endtemperatur von (850 ± 10) °C eingehalten werden kann;

i) elektrisch beheizter Muffelofen, mit dem eine Aufheizgeschwindigkeit von etwa 100 K/h und eine Endtemperatur von $(1\,300 \pm 10)$ °C eingehalten werden kann;

j) Temperaturmesseinrichtung (Thermoelement mit Anzeigeinstrument) zur Bestimmung der mittleren Probekörpertemperatur auf ± 5 K beim Brennen;

k) Blechbehälter (Saggar) mit Deckel zur Aufnahme der Probekörper;

l) Elektrographit als Packmasse mit einer Korngröße $\leq 0,8$ mm;

m) elektrisch beheizter Hochtemperaturofen, mit dem eine Aufheizgeschwindigkeit von etwa 50 K/min eingehalten, eine Endtemperatur von $(2\,800 \pm 50)$ °C erreicht und die Temperatur über die Länge der Probekörper auf ± 20 K konstant gehalten werden kann;

n) Temperaturmesseinrichtung (Strahlungspyrometer) zur Bestimmung der mittleren Probekörpertemperatur auf ± 20 K beim Graphitieren;

o) Steinkohlenteerpech mit einem Erweichungspunkt von (90 ± 5) °C nach Kraemer-Sarnow, bestimmt nach DIN 52025 oder (108 ± 5) °C nach Mettler nach DIN 51920;

p) Eisen(III)-oxid mit einem Massenanteil ω $(Fe_2O_3) > 85$ % und $\leq 0,075$ mm;

q) Presshilfsöl, paraffinisch;

r) Argon in Druckgasflasche als Schutzgas;

s) Stickstoff als Schutzgas.

4

5   Probenahme und Probenvorbereitung

Es wird eine Probe nach DIN 51701-2 entnommen und nach DIN 51701-3 vorbereitet. Die Probe wird bei (110 ± 5) °C bis zur Massenkonstanz getrocknet und im Exsikkator auf Raumtemperatur abgekühlt. Aus der getrockneten Probe wird die Einwaage entnommen.

6   Durchführung

6.1   Aufbereiten des Kokses

6.1.1   Kokskörnung A:

Etwa 500 g des Kokses werden mit der Labormühle auf eine Korngröße < 0,5 mm vermahlen und anschließend durch Sieben in die Korngrößen-Fraktionen < 0,071 mm und 0,071 mm bis 0,5 mm getrennt. Der Massenanteil des Kokses mit der Korngröße < 0,071 mm muss (60 ± 5) % betragen.

6.1.2   Kokskörnung B:

Etwa 500 g des Kokses werden vorgebrochen (ungefähr < 10 mm) und so lange mit einer Labormühle zerkleinert, bis der Massenanteil < 0,075 mm (52 ± 5) % beträgt.

Weitere etwa 1 500 g des Kokses werden mit einer Labormühle so lange grob gemahlen und gesiebt, bis mindestens je 80 g der folgenden Fraktionen erhalten werden: 6,7 mm bis 3,35 mm, 2,36 mm bis 1,18 mm und 0,85 mm bis 0,425 mm.

6.2   Mischen

6.2.1   Kokskörnung A:

Die Mischmaschine wird auf eine Temperatur von (135 ± 5) °C vorgeheizt. $(240 \pm 0,2)$ g Koks der Korngrößen-Fraktion < 0,071 mm und $(160 \pm 0,2)$ g Koks der Korngrößen-Fraktion 0,071 mm bis 0,5 mm werden zusammen mit $(8 \pm 0,2)$ g Eisen(III)-oxid in die Labormischmaschine gegeben und 5 min bei einer Temperatur von (135 ± 5) °C gemischt. Anschließend werden, je nach Bindemittelbedarf des Kokses, 136 g bis 148 g im Mörser grob zerkleinertes Steinkohlenteerpech dazugegeben und weitere 20 min bei (135 ± 5) °C gemischt. Zu dieser Mischung werden $(4 \pm 0,2)$ g Presshilfsöl gegeben. Danach wird nochmals 5 min bei (135 ± 5) °C gemischt. Die so erhaltene „grüne" Mischung wird in eine Porzellanschale gefüllt und im Wärmeschrank auf eine Temperatur von etwa 125 °C abgekühlt.

6.2.2   Kokskörnung B:

$(160 \pm 0,2)$ g der hergestellten Körnung < 0,075 mm (52 ± 5) % und $(8,5 \pm 0,2)$ g Eisen(III)-oxid werden mit einer Labormischmaschine vorgemischt. Anschließend werden jeweils $(80 \pm 0,2)$ g Koks der Fraktionen 6,7 mm bis 3,35 mm, 2,36 mm bis 1,18 mm und 0,85 mm bis 0,425 mm zugegeben und für weitere 15 min gemischt. Danach wird diese Mischung in einem Wärmeschrank auf etwa 200 °C aufgeheizt und etwa 1 h gehalten.

$(108 \pm 0,2)$ g Steinkohlenteerpech werden auf < 2 mm zerkleinert. Die Labormischmaschine wird auf (165 ± 5) °C vorgeheizt. Danach wird die vorstehend beschriebene Mischung mit dem Steinkohlenteerpech in die Labormischmaschine gegeben und 10 min bei geringer Geschwindigkeit gemischt. $(4 \pm 0,2)$ g Presshilfsöl werden zugegeben, dann wird etwa 5 min weiter gemischt. Die so erhaltene „grüne Mischung" wird in eine Porzellanschale gefüllt und im Wärmeschrank auf etwa 135 °C abgekühlt.

5

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6.3 Pressen

Der Massezylinder der Strangpresse wird auf eine Temperatur von (125 ± 5) °C, das Mundstück auf (105 ± 5) °C vorgeheizt. Der Massezylinder wird in die Vertikale geschwenkt und das Mundstück verschlossen. Anschließend wird die „grüne" Mischung aus dem Wärmeschrank in den Massezylinder gefüllt und der Massezylinder der Presse wieder in die Horizontale geschwenkt. Die „grüne" Mischung wird mit einem Druck von etwa 30 bar bis 100 bar (abhängig von der Koksart) ausgepresst, die Auspressgeschwindigkeit des Stranges sollte etwa 2 cm/min betragen. Der ausgepresste Strang wird in einer Rinne aufgefangen und auf Raumtemperatur abgekühlt. Die ersten 5 cm des Stranges werden verworfen, der Rest in Probekörper von 120 mm Länge geteilt.

ANMERKUNG Es kann zweckmäßig sein, die Mischung vor dem Auspressen vorzuverdichten. Dazu wird das Mundstück mit der Vorpressplatte verschlossen und die Mischung in etwa 2 min bis auf einen Druck von etwa 100 bar vorverdichtet.

6.4 Herstellung von graphitierten Probekörpern

6.4.1 Vorbrennen

Der Boden des Blechbehälters (Saggar) wird mit einer 3 cm bis 4 cm hohen Packmasseschicht bedeckt. Darauf werden die Probekörper gelegt. Der Abstand Blechbehälterwand zu Probekörper und von Probekörper zu Probekörper muss mindestens 2 cm betragen. Die Zwischenräume werden mit Packmasse ausgefüllt und die Probekörper 3 cm bis 4 cm hoch mit Packmasse überschichtet. Der Blechbehälter wird mit einem Deckel verschlossen und in den kalten Muffelofen eingesetzt. Die Probekörper werden mit folgenden Aufheizgeschwindigkeiten aufgeheizt:

Tabelle 1

Temperaturbereich	Aufheizgeschwindigkeit
Raumtemperatur bis 300 °C	25 K/h bis 30 K/h
über 300 °C bis 850 °C	70 K/h bis 75 K/h

Die Endtemperatur von (850 ± 10) °C wird 2,5 h beibehalten. Danach wird die Heizung abgeschaltet und der Blechbehälter mit den Proben im Ofen auf Raumtemperatur abgekühlt. Die vorgeglühten Probekörper werden von anhaftender Packmasse befreit.

6.4.2 Graphitieren

Die vorgeglühten Probekörper werden in den kalten Hochtemperaturofen eingesetzt und mit folgenden Aufheizgeschwindigkeiten aufgeheizt:

Tabelle 2

Temperaturbereich	Aufheizgeschwindigkeit
Raumtemperatur bis 1 200 °C	45 K/min bis 50 K/min
über 1 200 °C bis 1 900 °C	8 K/min bis 10 K/min
über 1 900 °C bis 2 800 °C	35 K/min bis 40 K/min

Die Endtemperatur von (2 800 ± 50) °C wird 30 min beibehalten.

6

Nach dem Abschalten der Heizung lässt man die Probekörper im Hochtemperaturofen auf Raumtemperatur abkühlen. Während des Aufheizens und des Abkühlens der Probekörper im Hochtemperaturofen wird mit Argon als Schutzgas gegen Abbrand gespült.

6.5   Herstellung von geglühten Probekörpern

Falls die Probekörper im geglühten Zustand untersucht werden sollen, wird der Brennprozess bis zu einer Endtemperatur von (1 300 ± 10) °C durchgeführt. Die Probekörper werden in gleicher Weise, wie in 6.4.1 beschrieben, in den Muffelofen eingesetzt.

Folgende Aufheizgeschwindigkeiten sind beim Aufheizen einzuhalten:

Tabelle 3

Temperaturbereich	Aufheizgeschwindigkeit
Raumtemperatur bis 300 °C	25 K/h bis 30 K/h
über 300 °C bis 850 °C	70 K/h bis 75 K/h
über 850 °C bis 1 300 °C	45 K/h bis 50 K/h

Die Endtemperatur von (1 300 ± 10) °C wird 1 h beibehalten. Während der gesamten Temperaturbehandlung einschließlich des Abkühlens wird mit Stickstoff gespült.

7   Prüfbericht

Im Prüfbericht ist mindestens Folgendes anzugeben:

a)   Hinweis auf diese Norm;

b)   Art und Bezeichnung der Probekörper einschließlich Angabe des verwendeten Kokses, Bindemittels und der Temperaturbehandlung (graphitiert oder geglüht);

c)   von dieser Norm abweichende, vereinbarte Bedingungen;

d)   Herstellerdatum.

7

DEUTSCHE NORM

April 1998

Prüfung von Kohlenstoffmaterialien
Bestimmung des linearen thermischen Ausdehnungskoeffizienten
Feststoffe

DIN

51909

ICS 71.060.10

Ersatz für
Ausgabe 1984-02

Deskriptoren: Kohlenstoffmaterial, Feststoff, Prüfung, Ausdehnungskoeffizient

Testing of carbon materials — Determination of coefficient of linear
thermal expansion — Solid materials

Essais des matériaux de carbone — Détermination du coefficient linéaire
d'expansion thermique — Matières solides

Vorwort

Die vorliegende Norm wurde vom Arbeitsausschuß NMP 281 „Prüfverfahren für Kohlenstoff und Graphit" ausgearbeitet.

Änderungen

Gegenüber der Ausgabe Februar 1984 wurden folgende Änderungen vorgenommen:

a) Durchführung des Verfahrens verbessert;

b) Verweise aktualisiert.

Frühere Ausgaben

DIN 51909: 1984-02

1 Anwendungsbereich

Diese Norm legt ein Verfahren zur Bestimmung des mittleren linearen thermischen Ausdehnungskoeffizienten von Kohlenstoff und Graphitmaterialien (Feststoffe) zwischen 20 und 1000 °C fest.

2 Normative Verweisungen

Diese Norm enthält durch datierte oder undatierte Verweisungen Festlegungen aus anderen Publikationen. Diese normativen Verweisungen sind an den jeweiligen Stellen im Text zitiert, und die Publikationen sind nachstehend aufgeführt. Bei datierten Verweisungen gehören spätere Änderungen oder Überarbeitungen dieser Publikationen nur zu dieser Norm, falls sie durch Änderung oder Überarbeitung eingearbeitet sind. Bei undatierten Verweisungen gilt die letzte Ausgabe der in Bezug genommenen Publikation.

DIN 862
   Meßschieber — Anforderungen, Prüfung

DIN 863-1
   Meßschrauben — Teil 1: Bügelmeßschrauben. Normalausführung, Begriffe, Anforderungen, Prüfung

DIN 1319-3
   Grundlagen der Meßtechnik — Teil 3: Auswertung von Messungen einer einzelnen Meßgröße, Meßunsicherheit

DIN 1333
   Zahlenangaben

[1] J. Otto und W. Thomas: Die thermische Ausdehnung von Quarzglas im Temperaturbereich von 0 bis 1060 °C, Z. f. Phys., 175 (1963), S. 334 bis 337

3 Definitionen

Für die Anwendung dieser Norm gelten die folgenden Definitionen:

3.1 Linearer thermischer Ausdehnungskoeffizient $\alpha(\vartheta)$

Maß für die Längenänderung eines Körpers in Abhängigkeit von der Temperatur,

$$\alpha(\vartheta) = \frac{1}{l} \cdot \frac{dl}{d\vartheta} \qquad (1)$$

Dabei ist:

l Länge des Probekörpers bei der Temperatur ϑ;

$\dfrac{dl}{d\vartheta}$ Änderung der Länge mit der Temperatur ϑ.

3.2 Mittlerer linearer thermischer Ausdehnungskoeffizient $\alpha(\vartheta_1, \vartheta_2)$

Mittelwert für ein bestimmtes Temperaturintervall.

Fortsetzung Seite 2 und 3

Normenausschuß Materialprüfung (NMP) im DIN Deutsches Institut für Normung e.V.

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$$\alpha(\vartheta_1;\vartheta_2)=\frac{1}{l_1}\cdot\frac{l_2-l_1}{\vartheta_2-\vartheta_1}=\frac{1}{l_1}\cdot\frac{\Delta l}{\Delta\vartheta} \quad\quad (2)$$

$$\Delta\vartheta=\vartheta_2-\vartheta_1 \quad\quad (3)$$

$$\Delta l=l_2-l_1 \quad\quad (4)$$

Dabei ist

ϑ_1 Untere Temperatur;

ϑ_2 Obere Temperatur;

l_1 Länge des Probekörpers bei der Temperatur ϑ_1;

l_2 Länge des Probekörpers bei der Temperatur ϑ_2.

4 Kurzbeschreibung des Verfahrens

Der mittlere lineare thermische Ausdehnungskoeffizient wird mit einem Schubstangen-Dilatometer bestimmt. Hierbei wird der Probekörper, der sich in einer Halterung aus Material geringer Wärmeausdehnung befindet (z. B. Kieselglas), in einem Ofen aufgeheizt und die Längenänderung über eine Schubstange nach außen auf ein mechanisches, optisches oder elektronisches Meßsystem übertragen.

Aus der gemessenen Längenänderung, der Ausgangslänge und der Temperaturänderung des Probekörpers wird unter Berücksichtigung der Ausdehnung der Probenhalterung und der Schubstange der mittlere lineare thermische Ausdehnungskoeffizient berechnet. Sofern nicht anders angegeben, wird die Bestimmung zwischen 20 und 200 °C durchgeführt.

5 Bezeichnung

Bezeichnung des Verfahrens zur Bestimmung des mittleren linearen thermischen Ausdehnungskoeffizienten von Kohlenstoff- und Graphitmaterialien (A):

Prüfung DIN 51909 — A

6 Geräte

- Dilatometer mit Probenhalterung und Schubstange, z. B. aus Kieselglas, sowie mechanischer, optischer oder elektronischer Längenänderungsmeßeinrichtung (Fehlergrenzen 0,05 μm) für Temperaturen über 300 °C mit Vakuum oder Schutzgaseinrichtung;
- Heizofen, mit dem die Temperatur über die Länge der Probekörper auf 0,5 % konstant gehalten werden kann;
- Temperaturmeßeinrichtung, z. B. Thermoelement mit Anzeigeinstrument mit Fehlergrenzen von 0,5 %, zur Bestimmung der mittleren Probekörpertemperatur;
- Längenmeßgerät mit Fehlergrenzen von 0,2 %, z. B. Meßschieber nach DIN 862 oder Bügelmeßschraube nach DIN 863-1, zur Bestimmung der Länge der Probekörper.

7 Probekörper

Verwendet werden zylindrische oder prismatische Probeköper, deren Durchmesser bzw. Querschnittskantenlänge mindestens gleich dem doppelten Durchmesser des größten Gefügebestandteils (z. B. maximale Korngröße) des zu untersuchenden Materials, jedoch nicht kleiner als 4 mm sein darf. Die Länge der Probekörper muß mindestens 25 mm, vorzugsweise jedoch 50 bis 120 mm betragen.

Die Probekörper werden allseitig, z. B. mit einer Dreh- oder Schleifmaschine, bearbeitet, wobei auf Planparallelität der Endflächen besonders zu achten ist.

ANMERKUNG: Eventuell auftretende Spannungen im Probekörper werden durch Wärmebehandlung bei 1000 °C in nichtoxidierender Atmosphäre beseitigt.

8 Durchführung

Die Ausgangslänge (Meßlänge) l_1 des Probekörpers wird bei der unteren Temperatur (Anfangstemperatur) ϑ_1 gemessen. Der Probekörper wird vor dem Einsetzen in das Dilatometer in der Mitte einer Längsseite mit einer etwa 1 mm tiefen Bohrung oder an der Stirnfläche, etwas außerhalb der Mitte, mit einer etwa 5 mm tiefen Bohrung für die Aufnahme der Lötstelle des Thermoelementes versehen. Beim Einbau des Probekörpers ist darauf zu achten, daß er mit seinen Stirnflächen an der Halterung und an der Schubstange fest anliegt. Falls die Kontaktflächen von Probenhalterung und Schubstange nicht kugel- oder kegelförmig ausgebildet sind, werden Zwischenstücke eingelegt, um einen möglichst punktförmigen Kontakt an den Stirnflächen des Probekörpers zu erreichen. Zu Beginn der Messung ist der Nullpunkt des Meßsystems einzustellen bzw. auf dem Registrier- oder Photopapier zu markieren, bei Doppeldilatometern, z. B. nach Bollenrath, mit zwei zueinander senkrechten Registriereinrichtungen außerdem auch die Lage der Achsen. Anschließend wird der Heizofen, der auch vorgeheizt werden kann, über die Probenhalterung geschoben. Nach Erreichen der oberen Temperatur (Endtemperatur) ϑ_2 ist der Meßwert abzulesen oder zu markieren.

Wird der Probekörper auf Temperaturen über 300 °C erwärmt, so muß durch Schutzgas oder Vakuum dafür gesorgt werden, daß keine Oxidation auftritt.

9 Auswertung

Der mittlere lineare thermische Ausdehnungskoeffizient in K^{-1} wird nach Gleichung (5) berechnet:

$$\alpha(\vartheta_1;\vartheta_2)=\frac{1}{l_1}\cdot\frac{\Delta l}{\Delta\vartheta}+\alpha_K \quad\quad (5)$$

$$\Delta l=l_2-l_1 \quad\quad (6)$$

$$\Delta\vartheta=\vartheta_2-\vartheta_1 \quad\quad (7)$$

Dabei ist

l_1 Länge des Probekörpers in mm bei der Temperatur ϑ_1;

l_2 Länge des Probekörpers in mm bei der Temperatur ϑ_2;

ϑ_1 Untere Temperatur in °C;

ϑ_2 Obere Temperatur in °C;

α_K Mittlerer linearer thermischer Ausdehnungskoeffizient in K^{-1} der Probenhalterung und der Schubstange für den bei der Bestimmung verwendeten Temperaturbereich [1].

Wenn nicht anders angegeben, gilt für die obere Temperatur $\vartheta_2=200$ °C, d. h., der lineare thermische Ausdehnungskoeffizient stellt den mittleren Wert für den Temperaturbereich von 20 bis 200 °C dar.

Bezüglich des Rundens auf die letzte anzugebende Stelle ist DIN 1333 zu berücksichtigen.

10 Prüfbericht

Im Prüfbericht sind unter Hinweis auf diese Norm anzugeben:

a) Art und Kennzeichnung der Probekörper;

b) Gegebenenfalls Vorbehandlung der Probekörper;

c) Anzahl der Probekörper;

d) Temperaturbereich der Messung;

e) Mittlerer linearer thermischer Ausdehnungskoeffizient in $10^{-6} K^{-1}$ auf $0,1 \cdot 10^{-6} K^{-1}$ gerundet.
Einzelwerte,
Mittelwert;

f) Von dieser Norm abweichende, vereinbarte Bedingungen;

g) Prüfdatum.

11 Präzision des Verfahrens

Die Meßunsicherheit dieses Prüfverfahrens beträgt für Probekörper mit einer Länge ≥ 50 mm bei Anwendung des Temperaturbereiches 20 bis 200 °C unter Wiederholbedingungen (siehe DIN 1319-3) auf einem Vertrauensniveau von 95 % etwa $0,05 \cdot 10^{-6} K^{-1}$ vom Meßwert.

Anhang A (informativ)

Literaturhinweise

DIN 51045-1
Bestimmung der thermischen Längenänderung fester Körper — Teil 1: Grundlagen

DIN 51045-2
Bestimmung der Längenänderung fester Körper unter Wärmeeinwirkung — Teil 2: Prüfung gebrannter feinkeramischer Werkstoffe

DIN 51045-3
Bestimmung der Längenänderung fester Körper unter Wärmeeinwirkung — Teil 3: Prüfung ungebrannter feinkeramischer Werkstoffe

DIN 51045-4
Bestimmung der Längenänderung fester Körper unter Wärmeeinwirkung — Teil 4: Prüfung gebrannter grobkeramischer Werkstoffe

DIN 51045-5
Bestimmung der Längenänderung fester Körper unter Wärmeeinwirkung — Teil 5: Prüfung ungebrannter grobkeramischer Werkstoffe

DIN 52328
Prüfung von Glas — Bestimmung des mittleren thermischen Längenausdehnungskoeffizienten

ASTM C 372
Test Method for Linear Thermal Expansion of porcelain Enamel and Glaze Frits and Fired Ceramic Whiteware Products by the Dilatometer Method
(Bestimmung der Wärmeausdehnung von Erzeugnissen aus Weißemail, Fritten sowie gebranntem Porzellan und Steingut)
Zu beziehen bei: Beuth Verlag GmbH, 10772 Berlin

[1] F. Kohlrausch, Praktische Physik, Stuttgart 1968, Bd. 1, D. 316 bis 319, Kap. 4.3.2 Wärmeausdehnung

[2] A. Metz, Ein neues Universal-Dilatometer nach Bollenrath, ATM 303 (1961) R 61 bis R 72

[3] P. Thormann, Dilatometeruntersuchungen auf dem Gebiet der keramischen Roh und Werkstoffe, Ber. dt. Keram. Ges. 46 (1969), S. 583 bis 588

[4] P. Thormann, Meßunsicherheit bei Dilatometeruntersuchungen und ihre Bedeutung in keramischen Laboratorien, Ber. dt. Keram. Ges. 47 (1970), S. 769 bis 773

Februar 2005

	DIN 51909 Berichtigung 1	**DIN**

ICS 71.060.10

> Es wird empfohlen, auf der betroffenen Norm
> einen Hinweis auf diese Berichtigung zu
> machen.

Berichtigungen zu DIN 51909:1998-04

Corrigenda to DIN 51909:1998-04

Corrigenda à DIN 51909:1998-04

Gesamtumfang 2 Seiten

Normenausschuss Materialprüfung (NMP) im DIN

DIN 51909 Ber 1:2005-02

In

DIN 51909:1998-04

Prüfung von Kohlenstoffmaterialien — Bestimmung des linearen thermischen Ausdehnungskoeffizienten — Feststoffe

ist folgende Korrektur vorzunehmen:

Im Abschnitt 6, erster Spiegelstrich, ist der Wert „0,05 µm" für die Fehlergrenze der Längenänderungsmesseinrichtung falsch angegeben. Richtig ist „0,5 µm".

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